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Raman scattering in silver borate glass doped with silver chloride

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Abstract : Raman spectra for the glasses 0.20 Ag_2O, 0.80 B_2O_3 and 0.20 AgCl, 0.80 (0.20 Ag_2O 0.80 B_2O_3) has been recorded at room temperature. The addition of AgCl in the binary binary silver borate glass results in the destruction of boroxol rings containing one or two BO_4 tetrahedra, together with the formation of small, highly charged units such as free BO_4, BO_3 *etc*

Keywords : Raman spectra, borate glass, scattering

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Borate glass containing various amounts of silver halides have been widely studied for their electrical properties and structure because of their high Ag^+ ionic conductivity and the potential usage of these glasses as solid electrolytes in batteries and other electrochemical devices [1-4]. However, the structural role of the halogens as anions in the borate glass has not yet been explained satisfactorily. IR and UV investigations on borate glasses containing alkali and alkaline-earth fluorides suggested that F^- ion is covalently bonded to boron atoms [5, 6]. Nishida *et al* [7] suggested on the basis of Mössbauer and ESR studies that the role of the halogens is dependent on the alkali content of the glass. Geissberger *et al* [3] proposed from NMR studies that halogen anions in the borate glass are present in the interstitial sites among the glass network structure as free ions.

The binary silver borate glass was prepared by heating the weighed amount of reagent grade silver nitrate and boric acid in electric furnace at 1100 K for an hour. Within experimental errors, gravimetric analysis showed that when the mixture was heated, its weight decreased as expected for complete ejection of water (from H_3BO_3) and nitrogen oxide (from $AgNO_3$). The sample was made by pouring the bubble free melt in between the

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stainless steel molds kept at room temperature. The sample was transparent, light brown in color and tend to darken on laser light exposure. This phenomenon was avoided by reducing the power of the laser falling on the sample to less than 100 mW. The ternary silver borate glass system was prepared by heating the weighed amounts of reagent grade silver nitrate, silver chloride and boric acid in electric furnace at 1200 K for an hour. This glass is transparent and greenish in color. No effect on this glass has been observed during its exposure to laser light. The metal oxide doped glasses are highly hygroscopic materials. Even at very high temperature, hydroxyl groups may be present in it. However, just after the preparation of the samples, these were kept in the desiccator which was provided with dry $CaCl_2$ to remove the last traces of water from inside. Extra care is needed for binary silver borate glass sample because of its photosensitive character. To avoid this process, the desiccator was covered with dark black clothe. Whenever the sample was used for scanning, the faces of the glass was again smoothened by carborundum powder and polished with soft cloth. The analysis of X-ray diffractogram shows that the samples are amorphous.

The Raman spectra at room temperature were recorded in our laboratory on a standard system consisting of Spectra Physics argon ion laser using 514.5 nm as the exciting line, a Jobin Yvon Ramanor U-1000 double monochromator with holographic gratings and a photon counting system. The spectra were recorded at conventional right angle scattering geometry. The laser power of 100 mW was used for recording the spectra.

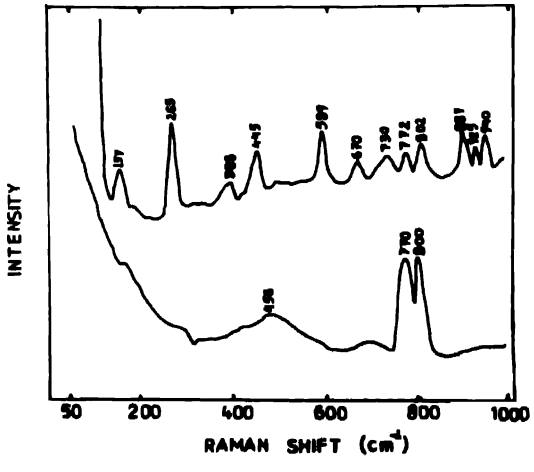

Figure 1. Raman spectrum of binary and ternary silver borate glass in the system (a) 0.20 Ag_2O. 0.80 B_2O_3 ; (b) 0.20 AgCl. 0.80 (0.20Ag_2O. 0.80 B_2O_3).

Raman spectra for the glasses 0.20 Ag_2O. 0.80 B_2O_3 and 0.20 AgCl. 0.80 (0.20 Ag_2O. 0.80 B_2O_3) are shown in Figure 1. The various possibilities regarding changes in the structure of the binary silver borate glass network on the addition of AgCl are given as :

(1) AgCl does not react with the borate glass network and no change in the network occurs. The relative amount of 4-coordinated boron N_4 is determined by the ratio Ag_2O/B_2O_3.

(2) Cl^- changes the coordination number of boron atom from 3 to 4 and is bonded to the 4-coordinated boron atom.

(3) Cl^- is bonded to the 3-coordinated boron and a certain amount of oxygen in the BO_3 unit is expelled out by Cl^-, resulting in BO_2Cl^- units. The oxygen will be consumed in the formation of additional BO_4 units.

The second and third processes bring the increase in the 4-coordinated B upon the addition of AgCl and N_4 is determined by the ratio $Ag_2(O + Cl_2)/B_2O_3$.

Soppe *et al* [8] concluded from the Raman study of lithium borate glasses doped with LiCl that the addition of LiCl does not produce any major modification in the vitreous boron-oxygen network. The addition of LiCl molecules in glasses with low Li_2O concentration leads to an increase of the density and the glass transition temperatrre [8,9]. On the basis of this fact Soppe *et al* [8] concluded that the large Cl^- ions are accommodated in the relatively open structure Because of the negative charge of the Cl^- ion, these are located at large distances from the BO_4^- charge groups. The Cl^- ions therefore do not produce strong interactions with the vibrations of the glass network. At higher Li_2O contents, the number of BO_4 groups increases and the structure is not as open as the structure of pure v-B_2O_3. As a result, it is more difficult to accommodate Cl^- ions in this structure. Thus, introduction of Cl^- ions leads to an expansion of the glass structure and a corresponding decrease of the density and the glass transition temperature

The role of AgCl in the binary silver borate glass system can be understood by a study of the change in its Raman spectra. The main observations in the present investigation are the growth of new bands at 589, 730, 887, 925 and 940 cm^{-1} upon adding the AgCl in the binary silver borate glass matrix At the same time, a change in the intensity of the 770 and 800 cm^{-1} bands is also observed. It is widely accepted that the band around 806 cm^{-1} arises due to the ring breathing vibration of the boroxol ring in which only oxygen atoms are involved in vibration rather than boron atoms [10]. The band around 770 cm^{-1} arises due to the same type of vibration but in which boroxol rings involving one or two BO_4 tetrahedra exist [11]. The decrease in the intensity of the bands around 770 and 800 cm^{-1}, together with the formation of some new bands which were not present in binary silver borate glass system, clearly indicates the glass modifying behaviour of AgCl.

In the case of binary silver borate glasses, two weak and broad bands located at 456 and 670 cm^{-1} (for $x = 0.20$) have been observed. The addition of AgCl in this glass matrix results in the increase in intensity and narrowing of these bands together with slight shift in the position of 456 cm^{-1} band. These bands are now placed at 445 and 670 cm^{-1}. In binary

silver borate glasses the band around 456 cm^{-1} has been assigned as arising due to the bending mode of vibration of free BO_4 unit or one that is attached very weakly to a ring type structure [12]. The increase in intensity of this band upon the addition of AgCl indicates that AgCl takes part in the destruction of borate rings containing one or two BO_4 tetrahedra, resulting in the formation of a large number of free BO_4 units. The decrease in intensity of the bands at 770 and 802 cm^{-1} upon addition of AgCl also confirms the above result. The weak band around 670 cm^{-1} has been assigned to a ring type metaborate [12].

An interesting result on the typical borate groups forming the glass network is deduced from the analysis of bands in the region 850-950 cm^{-1}. By comparison with the spectra of polycrystalline compounds, it is possible to attribute the band at 940 cm^{-1} to the B–O stretching in BO_4 units grouped to form polycrystalline diborate [13]. The band at 887 cm^{-1} correspond to the same bond vibration in tetraborate polycrystals [13]. The weak band located at 925 cm^{-1} confirms the presence of orthoborate groups at this glass composition. This band has been assigned to the $B–O^-$ bond stretching vibration in BO_3^- units [14].

A new feature located at 730 cm^{-1} arises upon addition of AgCl in binary silver borate glass. The Raman spectrum of crystalline B_2O_3 shows a band at 720 cm^{-1} [15]. According to Gurr *et al* [16] the network of crystalline B_2O_3 consists of chains of BO_3 triangles and does not contain boroxol rings. The same type of chain has been observed in crystalline $Li_2O.B_2O_3$. Thus it can be concluded that 730 cm^{-1} band in ternary silver borate glass system is attributed to a vibration of the chain type metaborate groups. The sharp and strong bands at 265 and 157 cm^{-1} are probably cation motion bands at high and low potential energy sites respectively. This assignment actually needs further investigation of ternary glass system over a wide compositional range.

Thus from the Raman scattering study of binary silver borate glass system doped with silver chloride, we may conclude that addition of silver chloride results in the destruction of borate rings containing one or two BO_4 tetrahedra, together with the formation of small, highly charged units such as free BO_4, BO_3^- *etc*. The presence of silver ions in adjacent to the anionic sites has also been confirmed from the two Raman bands at 265 and 157 cm^{-1} Chemically, one may expect that the silver ions (Ag^+) are placed adjacent to the BO_4^- and BO_3^- units to provide local charge neutrality. Addition of silver chloride, results in the formation of large number of free highly charged anionic sites and thus the possibility of accommodating silver ions (from AgCl) in adjacent to this anionic sites is quite likely. It has been reported that the addition of silver halide results in a sharp increase of ionic conductivity. Thus we may also expect the possibility of large number of free silver ions in the network.

On the basis of this mechanism, a structural model for the ternary silver borate glass in the present system is proposed in Figure 2. Non-bridging oxygens are present in BO_3 groups only. Three types of Ag^+ ions are illustrated; the first one Ag^+ ions bonded with non-bridging

oxygen with strong partial covalency, the second one Ag^+ ions surrounded with Cl^- ions, and the third one Ag^+ ions interacting with BO_4^- groups.

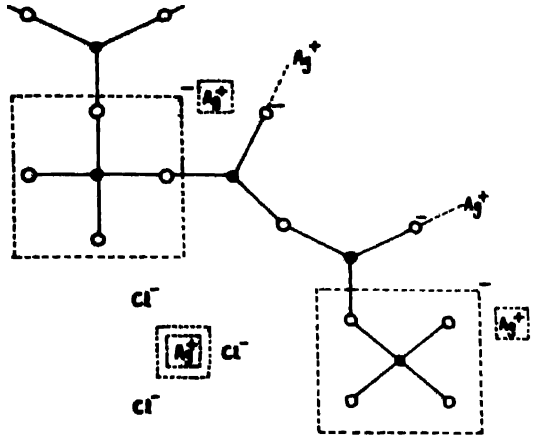

Figure 2. A proposed model for the glass structure in the system 0.20 AgCl 0.80 (0.20 Ag_2O. 0.80 B_2O_3).

● → boron, O → oxygen

The fact that not all the Ag^+ ions contribute to the conduction suggests that the first type of Ag^+ ions takes part very slightly in the ionic conduction. The second and third type of Ag^+ ions contribute much to the increase in ionic conductivity.

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